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THE REACTION OF HYDROGEN WITH OXYGEN ON A POLYCRYSTALLINE IRON SURFACE

by

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## ABSTRACT

We have studied the interaction between hydrogen and oxygen on a polycrystalline iron sample using Auger electron spectroscopy (AES) and mass spectrometry. A hydrogen permeation method was used. We found that chemisorbed oxygen cannot be removed by reaction with adsorbed hydrogen, while oxygen incorporated into the near surface region of the bulk is titrated rapidly, to leave a constant amount of (Chemisorbed) oxygen on the surface, independent of reaction temperature ( $625 \geq T(^{\circ}\text{K}) \geq 475$ ). All results, including both the titration data obtained by AES and the water formation and desorption rates determined by mass spectroscopy, could be interpreted with an overall activation energy of  $16.0 \pm 2.6$  Kcal/mole. Of this total energy,  $8.5 \pm 0.4$  Kcal/mole was determined to be due to the kinetics of hydrogen permeation through the iron sample.

The reaction of coadsorbed hydrogen and oxygen on iron surfaces is difficult to study in an ultrahigh vacuum environment because of the low probability of dissociative adsorption of hydrogen. As a consequence, large gas phase hydrogen exposures ( $\geq 10^6$  Langmuir) are required to obtain a measurable extent of reaction (1,2). We have circumvented this limitation by using a sample configuration in which atomic hydrogen reaches the surface of a clean, polycrystalline iron surface by permeation through the bulk of the sample. We have used this configuration to study the titration of adsorbed oxygen by permeating hydrogen, over a wide range of oxygen coverage, over the temperature range from 475 to 625K.

The uptake of oxygen on the clean iron surface was followed using Auger electron spectroscopy (AES). The total surface coverage was determined from the ratio of height of the instantaneous oxygen KLL Auger peak to that of the iron LMM peak from the clean surface. The chemical state of the adsorbed oxygen (chemisorbed or oxide) was determined from the shape of the iron MVV Auger peak, which shows a pronounced energy shift when oxide formation takes place. It was found that oxygen is incorporated into a chemisorbed state for exposures up to 2.0 to 2.5 Langmuir. Calibration of the Auger peak and comparison with other studies indicates that this represents an oxygen coverage of one monolayer(1).

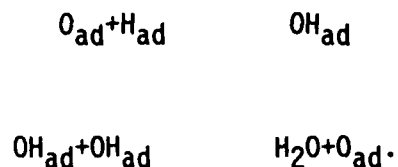
Further exposure to oxygen caused a shift in the Fe MVV Auger peak to approximately 43 eV, signaling the onset of oxide formation. During the initial stage of oxidation the rate of uptake was independent of the coverage and decreased with increasing substrate temperature, for up to approximately two monolayers of oxide. Uptake in this period was explained on the basis of a low temperature oxidation model formulated by Fehlner and Mott(3) and modified in this study(4). According to this

model, the post-chemisorption uptake of oxygen occurs on surface sites distinct from the chemisorption sites. The dissociative adsorption of oxygen on these sites is preceded by a molecular precursor and is followed by its non-activated incorporation into the subsurface region, resulting in oxide formation. On the basis of this model, the difference in the activation energies for the desorption and dissociation of the precursor was calculated to be 10 Kcal/mol. Further oxygen uptake was coverage dependent. Due to possible complications arising from the attenuation of the oxygen Auger peak intensity, the kinetics of adsorption or titration were not analyzed in this region.

When the surface was exposed to hydrogen permeating from the back side of the sample, pre-adsorbed oxygen was initially rapidly removed from the reaction surface, down to a constant residual amount of oxygen. The coverage of this untitratable oxygen was independent of both the substrate temperature ( $625 \leq T(^{\circ}\text{K}) \leq 475$ ) and the initial oxygen coverage, and corresponded to approximately 1 ML. Exposure of surfaces covered with less than this amount of oxygen to permeating hydrogen resulted in no water formation. The Fe MVV Auger peak observed for the untitratable species was typical of chemisorbed oxygen. Similar behavior has been observed by others for the titration by gas phase hydrogen of oxygen adsorbed on the (100) surface of iron (1).

A reaction scheme has been developed that excludes the chemisorbed oxygen from the overall titration process and has been successfully applied to the experimental data. This model assumes that a steady state hydrogen coverage is rapidly established on the surface, that the concentration of the titratable oxygen on the surface, ( $\theta_{\text{ad}}$ ), is always in equilibrium with the total amount of oxygen available for reaction,

that titration proceeds by initial hydrogenation of the  $O_{ad}$  species to form hydroxyl species, followed by a disproportionation step, leading to the formation and rapid desorption of water molecules:



It is also assumed that the concentration of the adsorbed hydroxyl species rapidly reaches a small, steady state value, and that this species is mobile. These assumptions are in qualitative agreement with both the experimental study of Dwyer et al. (5) and the theoretical work of Anderson (6).

All the titration data, as determined by AES, could be fit to the kinetic expression resulting from the above model. An Arrhenius plot of the apparent overall reaction rate constant versus temperature yielded an activation energy of approximately 16 Kcal/mol for the overall titration process. Out of this total energy, 8.5 Kcal/mol is due to the kinetics of hydrogen permeation in iron (7).

Similar experiments were performed using a quadrupole mass spectrometer (QMS) to monitor the desorption of water from the surface. The QMS signal at mass 18 was observed to rise rapidly, pass through a maximum and gradually decrease in intensity, at a rate dependent on the substrate temperature. Application of the reaction model described above to these data led to an identical value for the activation energy for  $H_2O$  formation. This confirms that the process is not perturbed by the primary electron beam of the Auger system and that the predominant reaction product is water.

Further experiments were performed under steady state hydrogen flow and constant gas-phase oxygen pressure conditions. At 500<sup>0</sup>K, the steady state (titratable) oxygen coverage on the surface varied according to  $(P_{O_2})^{1/2}$ , as would be expected from the above-defined oxidation and titration models (4).

Finally, it was found that the overall activation energy for oxygen titration increased by about 3 Kcal/mol with increasing initial surface oxygen coverage in the range between 1 and 3 ML. The reason for this behavior is not clear, through it may be due to an irreversible restructuring of the near-surface region of the substrate caused by the incorporation process. Such an effect might conceivably impede the return of the incorporated oxygen to the surface sites. It has been observed that annealing an oxidized Fe(100) surface also affects the overall titration rate(1).

#### ACKNOWLEDGEMENT

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